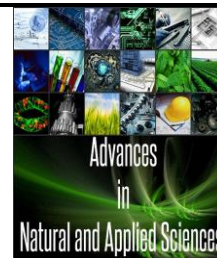




## Advances in Natural and Applied Sciences

ISSN:1995-0772 EISSN: 1998-1090  
Journal home page: [www.aensiweb.com/ANAS](http://www.aensiweb.com/ANAS)



### The Adsorption of Water Molecules on Titanium (iv) Oxide Surface as Studied by Near Infrared Spectroscopy

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#### ARTICLE INFO

##### Article history:

Received 3 August 2015

Accepted 28 October 2015

Available online 31 October 2015

##### Keywords:

cyclodextrins

NIR spectroscopy

Water adsorption

#### ABSTRACT

The adsorption properties of titanium (iv) oxide has been studied by near infrared spectroscopy and second derivative techniques. White titanium (iv) oxide sample was dried and allowed to adsorb water at a relative humidity of 40%. Its evolving near infrared spectra during the adsorption of water were measured and analysed using second derivative techniques. Furthermore, titanium (iv) oxide was hydrated at 160 and 220 °C and the variation in adsorptive properties of the resulting materials have been determined by gravimetric method. The analysis of the spectra confirms the presence of OH groups on the surface of titanium (iv) oxide. Furthermore the acquisition of water by titanium (iv) oxide takes place in two steps. The first step involves acquisition of free water molecules and adsorption of water molecules by hydrogen bonding. The second step involves adsorption of water molecules by hydrogen bonding to Ti-OH groups and bridging of the adsorbed water molecules adsorbed onto the Ti-OH groups. The gravimetric analyses show that the titanium (iv) oxide hydrated at 220 °C adsorbed less amount of water compared to the surface hydrated at 160 °C. This may indicate the formation of new OH groups and increasing the hydrogen bonded network of the Ti-OH groups on the surface.

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**To Cite This Article:** Alfred A. Christy., The Adsorption of Water Molecules on Titanium (iv) Oxide Surface as Studied by Near Infrared Spectroscopy. *Adv. in Nat. Appl. Sci.*, 9(14): 14-19, 2015

#### INTRODUCTION

Titanium (iv) oxide has become one of the important materials in several different fields including medicine, dentistry, photocatalysis etc (Tilocca and Selloni, 2003; 2004a; 2004b). It has also been a valuable material in paper and paint industry. The inertness and stability of the oxide makes it a better alternative in medical applications. Bones and dental implants of titanium (iv) oxide are very common nowadays. Titanium (iv) oxide exists in three different forms namely anatase, rutile and brookite. The first two are crystalline with tetragonal structure and brookite is orthorhombic. Rutile is the most stable form of titanium (iv) oxide. The white colour brightness, high opacity and strength of anatase and rutile make them excellent filler materials for paper mill industries. However, titanium (iv) oxide is highly abrasive and expensive and hence its uses are limited. Titanium (iv) oxide is also a semiconductor which photocatalyses the degradation of environmentally harmful organic compounds (Madjene *et al.*, 2013)

The behaviour of titanium (iv) oxide in several applications are attributed to its electronic, optical and surface properties. The enormous number of applications require the need to understand the

properties of titanium (iv) oxide. Adsorption properties of titanium (iv) oxide led to a great number of studies of its surface. Titanium (iv) oxide surface is the most studied surface of any metal oxide.

Like other polar surfaces, titanium (iv) oxide has the tendency to adsorb polar molecules including water molecules. Adsorption of water molecules on titanium (iv) oxide has been studied by several authors (Tilocca and Selloni, 2003, 2004a and 2004b; and Diebold, 2003). Christy in a series of articles (Christy, 2010, 2011a, 2011b, 2013a and 2013b) has given some insight on the surface hydroxyl groups and the way they adsorb water molecules. These articles have helped to reveal the different OH groups on certain material surfaces. The analytical technique used in these studies has been near infrared spectroscopy. In addition derivative techniques have been used in resolving and revealing different OH groups on different surfaces.

The aim in this article is to use the above mentioned analytical method and data analytical methodology to analyse the surface of titanium oxide. The analysis would reveal the type of OH groups present on the surface of titanium (iv) oxide and reveal how the adsorption of water molecules proceeds on the surface.

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The hydration experiments were carried out to check whether it is possible to introduce new OH groups on the surface and thereby affect the adsorption properties of the surface.

## MATERIALS AND METHODS

Titanium (iv) oxide was purchased from Sigma Aldrich. A ceramic heater (BA electric Bunsen from Electrothermal, UK) controlled by an external power supply was used in heating the samples. The temperature of the sample was measured by using a digital thermometer with a K type thermocouple (Clasohlson, UK). A powerful vacuum pump (Edwards, UK) was used in the evacuation of the samples.

The near infrared measurements were made using a PerkinElmer Spectrum One NTS FT-NIR spectrometer (Perkin Elmer Ltd, UK) equipped with a PerkinElmer transmittance accessory and deuterated triglycine sulphate detector. A sample of titanium (iv) oxide was placed in a glass vial with screw cap containing an air tight septum. The vial was then placed directly on the crystal of the transmittance accessory and the near infrared spectrum of the sample was measured in the region  $10,000\text{--}4000\text{ cm}^{-1}$  at a resolution of  $16\text{ cm}^{-1}$ . A total of 30 scans were made each time. The glass vial was then evacuated at  $260\text{ }^{\circ}\text{C}$  for 30 minutes, cooled and allowed to adsorb water molecules from a humidity controlled atmosphere. The relative humidity during the water adsorption experiments and near-infrared measurements of titanium (iv) oxide were controlled by a glycerol/water system (Forney and Brandl., 1992). The adsorption experiments and infrared measurements were carried out at a humidity of 40% and at a temperature of  $25.5\text{ }^{\circ}\text{C}$ . The NIR spectra of the sample were acquired using the same parameters. The reflectance spectra of the samples so obtained were converted to  $\log(1/R)$  format and saved. The spectra of the samples in  $\log(1/R)$  format were derivated twice and saved (Christy, 2010). These spectra were used in the detailed analysis of the surface of titanium (iv) oxide.

The hydration of titanium (iv) oxide was carried out in steel bomb of 25 cm in length and 1 cm in internal diameter. One gram of dry titanium (iv) oxide and  $1.0\text{ cm}^3$  of distilled water were added to the bomb and sealed. The bomb was then placed in a chromatographic oven set to  $160\text{ }^{\circ}\text{C}$  and left for two hours. The hydrated sample was removed, ground in a mortar and evacuated at  $260\text{ }^{\circ}\text{C}$  to remove physically adsorbed water from the surface. Another portion of dried titanium (iv) oxide was hydrated at  $220\text{ }^{\circ}\text{C}$ . Each hydrated sample was then transferred to a glass tube in which they were dried under vacuum. The quantitative adsorption of water

by the hydrated samples were then recorded by quickly spreading around 0.15g of each of the sample on a near infrared sample cup and placing it on an analytical balance that can record a weight change of 0.0001g. The weight of the sample was recorded continuously over a period of 2 hours.

## RESULTS AND DISCUSSION

The near infrared spectra of dry titanium (iv) oxide sample and the sample after adsorption of water for a little more than 20 hours are given in Fig. 1. A collection of near infrared spectra of the titanium (iv) oxide sample acquired during the adsorption of water molecules are given in Fig. 2. Second derivative spectra of the spectra in Fig. 2 are shown in Fig. 3.

The Fig. 1 clearly shows a sharp peak at  $7320\text{ cm}^{-1}$ . This peak is due to the first overtone of the OH groups on the surface of the titanium (iv) oxide. Like  $\text{SiO}_2$ , titanium (iv) oxide also forms hydroxyl groups on the surface by dissociation (Tilocca and Selloni, 2003). These surface OH groups are polarised because of the high electronegativity of oxygen atom and can adsorb water molecules by forming hydrogen bonds. This adsorption process is clearly evident in the spectrum acquired (shown in Fig. 1) on the dry sample after exposing it to surrounding air. The first overtone absorption of the OH group attached to titanium atom moves to a lower wavenumber.

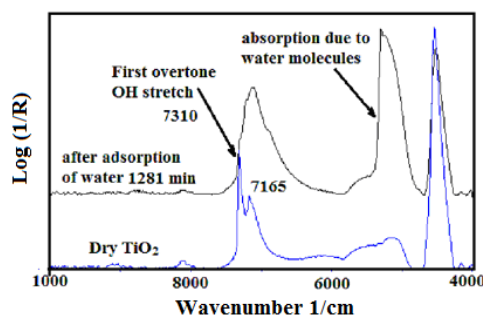
The band assignment of the titanium (iv) oxide with adsorbed water molecules are given in Table 1. The table gives OH related absorptions. The combination band of the OH stretching and OH bending of water molecules appearing in the region  $5400\text{--}5250\text{ cm}^{-1}$  are shown in Fig. 3.

These spectra show clearly the differences in water molecules adsorbed onto the surface. The combination frequency of the water molecules entering the system in the beginning had the same frequency as free water molecules ( $5282\text{ cm}^{-1}$ ). The water molecules are then adsorbed by the Ti-OH groups by forming hydrogen bonds. There is only one absorption peak in this region and therefore there is only one type of Ti-OH groups on the surface. It appears that the silanol groups in silica surface are closer than the Ti-OH groups on the titanium (iv) oxide surface. It means that there are no inter-hydrogen bonded Ti-OH groups on the surface. The Ti-OH groups are not close enough to form hydrogen bondings (Fig. 4).

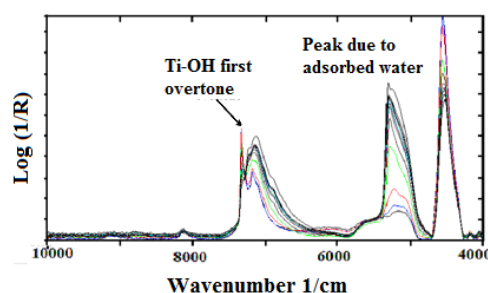
The intensity of absorption of the peak arising in the combination frequency region is proportional to the water molecules adsorbed by the titanium (iv) oxide sample. The same proportionality is true for the second derivative or the fourth derivative of the peak (Christy, 2010). A plot showing the relationship between the intensity of the fourth derivative of the combination frequency peak of the water molecules

and time is shown in Fig. 5. It appears that the water acquisition by titanium (iv) oxide takes place in two different steps. The absorption peak position at the start (in Fig. 3) shows that the water molecules acquired by the Ti-OH are in free form. The near infrared spectroscopy cannot give any explanation for the acquisition of free water molecules by titanium (iv) oxide. This is purely structure related. Then there is a blue shift in the frequency of the combination

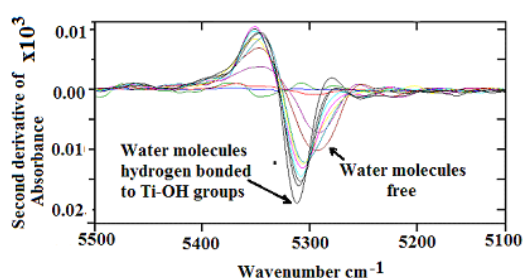
absorption and this indicates that the surface starts acquiring water molecules by adsorption. The adsorbed water molecules have weaker hydrogen bondings compared to the hydrogen bondings in Water. This leads to comparatively stronger OH bonds in the adsorbed water molecules and the frequency of absorption of the combination frequency experiences a blue shift.



**Fig. 1:** Near infrared spectra of dry titanium (iv) oxide and water adsorbed titanium (iv) oxide.



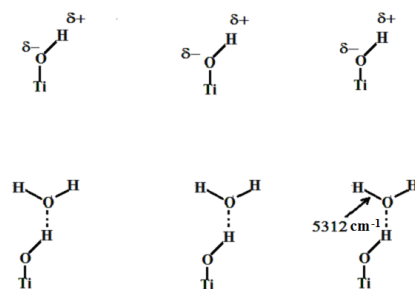
**Fig. 2:** Near infrared spectra of titanium (iv) oxide acquired during adsorption of water molecules at 40% relative humidity (0,19,35,60,80,106,115, 124,127,147 and 159 min. Exposure)



**Fig. 3:** Second derivative profiles of the spectra acquired during the adsorption of water molecules by titanium (iv) oxide shown in the region 5300-5200  $\text{cm}^{-1}$  (0, 19, 35, 60, 80, 106, 115, 124, 127, 147 and 159 min. Exposure).

**Table 1:** Band assignment for water adsorbed titanium (iv) oxide.

Peak ( $\text{cm}^{-1}$ )	Band assignment
7316 7225- 6860	Overtone-OH stretchings- Ti-OH groups Ti-OH hydrogen bonded to water molecules Water molecules hydrogen bonded to Ti-OH groups, water molecules hydrogen bonded to other water molecules
5312	Combination band OH stretching and bending of water molecules hydrogen bonded to Ti-OH groups

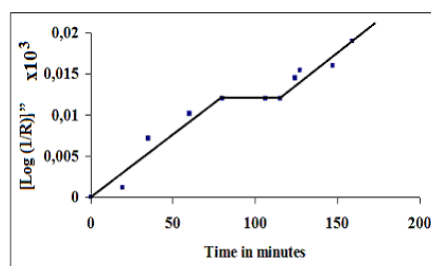


**Fig. 4:** Water molecules hydrogen bonded to Ti-OH groups.

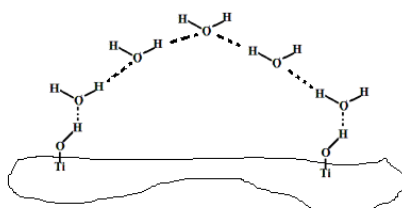
The adsorption of water molecules take place as shown in Fig. 4. When the Ti-OH groups are hydrogen bonded with water molecules, the adsorption reaches a plateau and the surface becomes inactive for some minutes before the adsorption of water molecules start again. The water molecules adsorbed during the second stage are bridging water molecules (Fig. 6).

The quantitative adsorption of water by dry and hydrated and dried samples are shown in Fig. 7 for

OH first overtone region. The spectra clearly show that the untreated titanium (iv) oxide has high concentration of free OH groups compared to hydrated and dried samples. The second derivative profiles of the absorption spectra of the samples measured during their water adsorption are shown in Fig. 8. There is one feature that is common for all the samples. The water acquired during the first exposure of the dry samples are free water molecules.



**Fig. 5:** Acquisition of water molecules by TiO<sub>2</sub> sample.



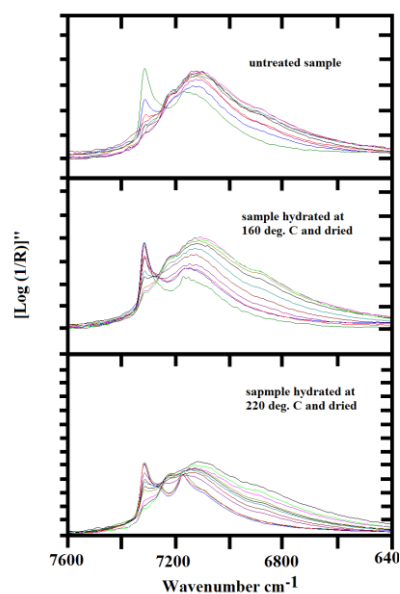
**Fig. 6:** Adsorption of bridging water molecules by water molecules hydrogen bonded to Ti-OH groups.

The adsorption of water determined by gravimetry are shown in Fig. 9. The hydration treatment of titanium oxide at 160 °C did not make any significant change in the adsorption properties of the surface of titanium (iv) oxide. This shows that the introduction of new OH groups in the titanium oxide matrix is difficult at this temperature of hydration. However, the sample hydrated at 220 °C adsorbs less water. The hydration at this temperature with the set up used in this experiment was able to introduce new OH groups. Some of the new Ti-OH groups introduced into the surface enter into hydrogen bondings with neighbouring Ti-OH groups

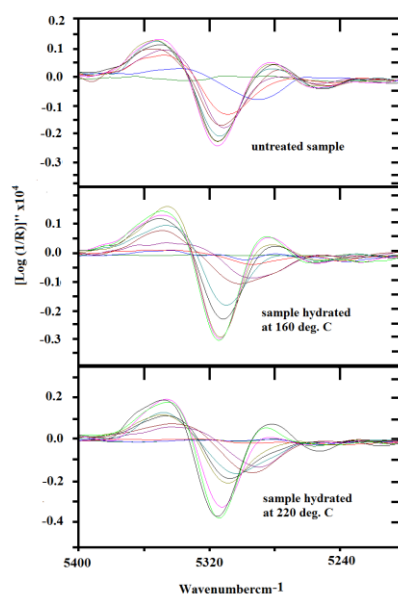
(Fig. 10) and reduce the number of OH groups available for hydrogen bondings with water molecules. This is exactly parallel to the behaviour of silica gel which loses its tendency for adsorbing water molecules after hydrothermal treatment [Christy, 2011b].

#### Conclusion:

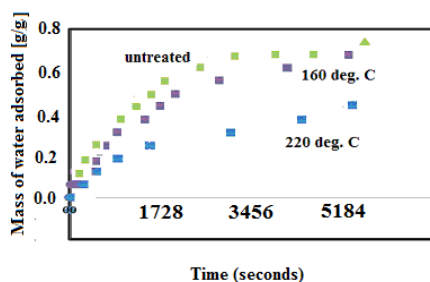
The near infrared spectroscopy and second derivative techniques seem to be valuable techniques in identifying the nature of water molecules adsorbed on surfaces.



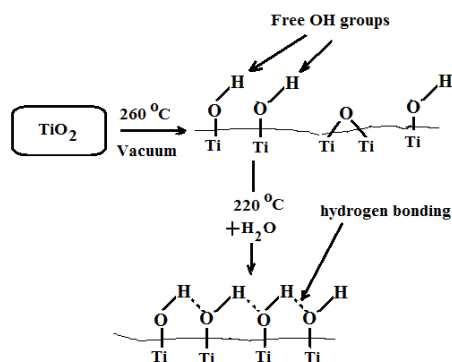
**Fig. 7:** The near infrared absorption spectra acquired during the adsorption of water on the dry samples, on samples hydrated at 160 °C and dried and on samples hydrated at 220 °C and dried.



**Fig. 8:** Near infrared second derivative spectra for the samples in 5400-5100  $\text{cm}^{-1}$  region.



**Fig. 9:** Water adsorbed by treated and untreated titanium (iv) oxide samples determined by gravimetry.



**Fig. 10:** Figure showing the formation of new OH group in the hydrated titanium (iv) oxide sample.

The results show that the surface of Titanium (iv) oxide has OH groups that are formed by dissociation and they are hard to eliminate at the drying temperature used in this experiment. Furthermore, the analysis also confirms that there is no infrared spectroscopic evidence for the inter-hydrogen bonding between two Ti-OH groups on the surface.

The adsorption evolution of water studied in this work show that the water acquired by the Titanium (iv) oxide surface are free water and adsorbed water. The acquisition of water molecules in both steps take place rapidly. The water acquisition processes are the same even after hydration of the sample.

The hydration experiments and the analyses show that new hydroxyl groups can be introduced by treating Titanium (iv) oxide with water in steel bombs at temperatures above 220 °C. The steam produced reacts and open Ti-O-Ti bonds to form new OH groups.

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